PREPARATION OF BIODIESEL FROM WASTE COOKING OIL AND REFINES BLEACHED DEODORIZED OIL USING SINGLE STEP BATCH TRANSESTERIFICATION PROCESS WITH THE AID OF KOH AS THE CATALYST

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ABSTRACT

Biodiesel is a cleaner burning diesel replacement fuel processed from natural, renewable derived from biological sources such as waste cooking oil and refined bleached deodorized palm oil. The type of process that needs to be done to produce biodiesel is called transesterification. The transesterification of waste cooking oil and refined bleached deodorized palm oil with short-chain alcohols, in the presence of base-catalyst potassium hydroxide (KOH) and methanol as solvent, by means of single step batch transesterification process in order to obtain biodiesel fuel was studied. The reaction has been done in water bath. The process variables that been investigated are catalyst concentration and reaction time. The variables that are fixed throughout the whole experiment were molar ratio of methanol to raw oil with 6: 1, reaction temperature at $40^{o}C$ and mixing degree of mechanical stirrer at 1300 rpm. This paper also studied the combustion characteristic which is the carbon monoxide emission between WCO and RBD to be compared with conventional diesel, and determined the optimal transesterification reaction conditions that produce the maximum methyl ester content or purity and biodiesel yield. The best result for highest yield and highest purity is at 60 minutes reaction time and using 1.5% catalyst concentration

ABSTRAK

Biodiesel adalah sumber minyak yang lebih bersih yang boleh menggantikan diesel dan boleh didapati dari sumber biologi yang semulajadi seperti minyak masak terpakai dan minyak masak kelapa sawit. Proses yang diperlukan untuk menghasilkan biodiesel dipanggil transesterifikasi. Proses transesterifikasi dijalankan untuk minyak masak terpakai dan juga minyak masak kelapa sawit dengan campuran pemangkin alkali iaitu Kalium Hidroksida (KOH) dan methanol sebagai pelarut. Tindakbalas ini di lakukan di dalam besen air. Proses ini dinamakan proses transesterifikasi langkah pertama untuk mendapatkan biodiesel. Faktor-faktor yang mempengaruhi transesterifikasi trigliserida adalah seperti kepekatan pemangkin dan tindakbalas masa akan dikaji. Factor-faktor yang telah ditetapkan sepanjang eksperimen adalah nisbah molar methanol kepada minyak iaitu 6:1, tindakbalas suhu pada $40^{o}C$ dan juga darjah kacauan sebanyak 1300 rpm oleh pengacau mekanikal. Kertas kajian ini juga mengkaji ciri-ciri pembakaran iaitu pembebasan karbon monoksida antara minyak masak terpakai dan minyak sawit mentah dengan diesel. Selain itu, kondisi tindakbalas transesterifikasi yang optima yang menghasilkan kandungan kepekatan metal ester dan kadar hasilan biodiesel yang optima juga akan dikaji. Keputusan terbaik diperoleh pada masa tindakbalas 60 minit dan kepekatan pemangkin pada 1.5%.

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LIST OF ABBREVIATIONS

°C	Degree celcius
FFA	Free fatty acid
h	Hour
min	minutes
g	gram
kg	kilogram
L	Liter
ml	mililiter
ppm	parts per million
KOH	Potassium Hydroxide
WCO	Waste Cooking Oil
WVO	Waste Vegetable Oil
RBD	Refined Bleached Deodorized Oil
FAME	Fatty acid methyl ester
NOx	Nitrogen Oxide
CO_2	Carbon Dioxide
HC	Hydrocarbon

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The world consumption of fuels is undoubtedly unstable causing world economic crisis; the worst compared to other economic recession that took place at different era. This factor has urged all nations especially the government and the academics to find another alternatives to replace the usage of petroleum. Therefore there is a rising demand to globally provide renewable energy by means of a sustainable and ethical approach. Sustainable development is a concept that has become significant and increases the awareness of its necessity.

There are many alternatives nowadays. There is three generation of biofuel. First-generation biofuels are biofuels made from sugar, starch, vegetable oil, or animal fats using conventional technology. These feedstocks could instead enter the animal or human food chain, and as the global population has risen their use in producing biofuels has been criticised for diverting food away from the human food chain, leading to food shortages and price rises. Second generation biofuel production processes are in development. These allow biofuel to be derived from any source of biomass, not just from food crops such as corn and soy beans but also from waste cooking oil. Algae fuel, also called oilgae or third generation biofuel, is a biofuel from algae.

1.2 Background of Study

Biodiesel is a fuel made from natural, renewable sources, such as new and used vegetable oils and animal fats, for use in a diesel engine. Biodiesel has physical properties very similar to petroleum-derived diesel fuel, but its emission properties are superior. Using biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromtic hydrocarbons, and particulate matter. Diesel blends containing up to 20% biodiesel called B20 can be used in nearly all diesel-powered equipment, and higher-level blends and pure biodiesel, B100 can be used in many engines with little or no modification. Lower-level blends are compatible with most storage and distribution equipment, but special handling is required for higher-level blends.

One of the most used renewable energy is biodiesel which is the most common biofuel in Europe. It is produced from oils or fats using transesterification and is a liquid similar in composition to mineral diesel. Its chemical name is fatty acid methyl ester (FAME). In our study, oils are mixed with potassium hydroxide KOH as catalyst and methanol and the chemical reaction produces biodiesel (FAME) and glycerol. 1 part glycerol is produced for every 10 parts biodiesel.

Biodiesel can be used in any diesel engine when mixed with mineral diesel. In some countries manufacturers cover their diesel engines under warranty for 100% biodiesel use. Many people have run their vehicles on biodiesel without problems. However, the majority of vehicle manufacturers limit their recommendations to 15% biodiesel blended with mineral diesel. In many European countries, a 5% biodiesel blend , B5 is widely used and is available at thousands of gas stations. Biodiesel can be made from waste and virgin vegetable and animal oil and fats (lipids). Virgin vegetable oils can be used in modified diesel engines. In fact the diesel engine was originally designed to run on vegetable oil rather than fossil fuel. There are also studies and efforts to commercialize biodiesel from algae.

1.3 Problem Statement

Petroleum price is undoubtedly agreed to be very unstable. At some point the price roars to maximum price at $145 per barrel. Then it decrease till $40 per barrel. This sort of trend has affected the world economic growth. Each human being in this mother earth can feel the effect of economic crisis that is mainly caused by unstable price of petroleum. Thus, by using biodiesel as alternative, the problem could be tackle.

Malaysia is famously known as one of the nett producer of palm oil. It has the potential to lead the way in biofuel production looking at its vast production of palm oil. By using Refined-Bleached-Deodorized (RBD) palm oil, Malaysian would have a consistent supply and provision to replace the usage of diesel petroleum. Besides palm oil is also one of the most highly efficient feedstock for biodiesel compared to other vegetable oils. (Ang, Catharina Y. W., KeShun Liu,et al, 1999)

Another raw material that will be use in the research is waste cooking oil. It seems as a practical way for waste cooking oil (WCO) to be converted as biodiesel as it will give a comparable and cheap price than subsidized diesel. Furthermore, the usage of waste cooking oil will promote into a cleaner environment because the water and land will be less polluted by waste cooking oil. But the main problem of using waste cooking oil is the existence of free fatty acid as the by product in transesterification process.

Thus the aim of this project is to produce biodiesel as diesel substitute at a feasible way. The research of which types of feedstock is the best have to be conduct. The result of the study will provide a clear picture as to which feedstock will be sustainable in alleviating the energy crisis.

Single step transesterification process will be used in synthesizing raw material to methyl ester. Single step transesterification process provides less time in reaction, lower temperature and pressure, and hence will result in less cost of production. The high content of free fatty acid in waste cooking oil need to be synthesize by using homogenous catalyst, Potassium Hydroxide (KOH). Even though the use of homogenous catalyst resulted in higher formation of soap, homogenous catalyst provides shorter reaction time compare to heterogeneous. In the transesterification process, methanol will be use as alcohol solvent because of its price is cheaper among other alcohol solvent.

1.4 Objective

Aim of this project is to determine the best condition in producing biodiesel with high purity of methyl ester and environmental friendly biodiesel, from Refined Bleached Deodorized palm oil and Waste Cooking Oil by using single step batch transesterification process.

1.5 Scope of Research

In order to achieve the objective, three scopes have been identified to be studied in this experiment. They are:

i. To study the effect of catalyst concentration and reaction time from both Refined-Bleached-Deodorized (RBD) palm oil and waste cooking oil (WCO) by using single step transesterification process.
ii. To analyze methyl ester concentration or purity by using Gas Chromatography.
iii. To compare the combustion characteristic of biodiesel produced from both Refined-Bleached-Deodorized (RBD) palm oil and waste cooking oil (WCO) with standard diesel by usong gas analyzer.

In the research that will be conducted, we will fix the temperature at 40°C. While the catalyst concentration used is between 0.5, 0.75, 1.0 and 1.5wt% and the time that be conducted is from 30, 40, 50 and 60 minutes.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to American Society for Testing and Materials, ASTM D6751 specifications for use in diesel engines. It is a clean burning alternative fuel, produced from domestic, renewable resources. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Biodiesel is made through a chemical process called transesterification whereby the glycerin is separated from the fat or vegetable oil. The process leaves behind two products: methyl esters or biodiesel and glycerin.

Biodiesel is much cleaner than fossil-fuel diesel. It can be used in any diesel engine with no need for modifications. In fact diesel engines run better and last longer with biodiesel. And it can easily be made from common waste product, used cooking oil. Biodiesel is better for the environment because it is made from renewable resources and has lower emissions compared to petroleum diesel (UNH Biodiesel Group). It is less toxic than table salt and biodegrades as fast as sugar.

2.1.1 Biodiesel emission and engine relation

A major benefit of biodiesel is lower emissions. The use of biodiesel reduces emission of carbon monoxide and other hydrocarbons by 20 to 40%. Biodiesel burns up to 75% cleaner than conventional petroleum diesel fuel. Biodiesel reduces unburned hydrocarbons (-93%), carbon monoxide (-50%) and particulate matter (-30%) in exhaust fumes, as well as cancer-causing PAH (-80%) and nitrited PAH compounds (-90%). (US Environmental Protection Agency).

Sulphur dioxide emissions are eliminated as biodiesel contains no sulphur. Biodiesel is plant-based and using it adds no extra CO_2 to the atmosphere. The ozone-forming (smog) potential of biodiesel emissions is nearly 50% less than petro-diesel emissions. Nitrogen oxide (NOx) emissions may increase or decrease but can be reduced to well below petrol-diesel fuel levels. Biodiesel exhaust is not offensive and does not cause eye irritation. Biodiesel is environmentally friendly, it is renewable, "more biodegradable than sugar and less toxic than table salt" (US National Biodiesel Board, based on US Environmental Protection Agency studies).

Biodiesel is a much better lubricant than petro-diesel and extends engine life. Even a small amount of biodiesel means cleaner emissions and better engine lubrication. 1% biodiesel added to petro-diesel will increase lubricity by 65% (UNH Biodiesel Group). Biodiesel can be mixed with petrol-diesel in any proportion, with no need for a mixing additive. Biodiesel has a higher cetane number than petroleum diesel because of its oxygen content. The higher the cetane number the more efficient the fuel, the engine starts more easily, runs better and burns cleaner. With slight variations depending on the vehicle, performance and fuel economy with biodiesel is the same as with petrol-diesel.

2.1.2 Biodiesel Properties

Table 2.1 shows a comparison of chemical properties and fatty acid composition (%) of WCO and RBD palm oil. Both results are varies. Fatty acid is a carboxylic acid often with a long unbranched aliphatic tail (chain). These long-chain fatty acids generally have an even number of carbon atoms; unbranched chains predominate over branched chains. They may be saturated (e.g. palmitic (hexadecanoic) acid and stearic (octadecanoic) acid) or unsaturated, with one double bond (e.g. oleic (cis-octodec-9-enoic) acid) or two or more double bonds, in which case they are called polyunsaturated fatty acids (e.g. linoleic acid and linolenic acid). As for specific gravity, WCO has higher specific gravity because it has much residue such as water as water has mixed inside the WCO as a result of condensation of cooking process. So, the density of WCO is higher compared to RBD palm oil.

Table 2.1: Comparison of chemical properties and fatty acid composition (%) of WCO and RBD palm oil

Property	**WCO**	**RBD Palm oil**
Palmitic acid C16:0	16	44.3
Stearic acid C18:0	5.21	4.6
Oleic acid C18:1	34.28	38.7
Linoleic acid C18:2	40.76	10.51
Specific gravity	0.92	0.88

Table 2.2 shows major properties comparing between premium diesel and B100. The density for biodiesel is among 0.86 g/mL for RBD to 0.92 g/mL for WCO. Flash point is the temperature at which the vapour above a volatile liquid forms a combustible mixture with air. At the flash point the application of a naked flame gives a momentary flash rather than sustained combustion, for which the temperature is too low. So from

the table shown, biodiesel has higher flash point and it makes as an advantage because it would not easily vaporized to air compared to premium diesel. This will save the cost of fuel for transport especially if the temperature ambient is high. As for cetane number, a higher cetane number indicates greater fuel efficiency (Ya-fen Lin, Yo-ping Greg Wu and Chang-Tang Chang, 2006). In this case, B100 scores higher cetane number and it shows that the performance rating of a diesel fuel, corresponding to the percentage of cetane in a cetane-methylnaphthalene mixture with the same ignition performance.

Table 2.2: Major properties of premium diesel and biodiesel used in this study

	Premium diesel	**B100**	**Test method**
Density at 20 °C (g/mL)	0.826	0.86	ASTM D 1298
Kinematic viscosity at 40 °C (cSt)	2.73	4.49	ASTM D 445
Cetane index	46.2	48.05	EN ISO 4264
Flash point (°C)	89	122	ASTM D 93
Water and sediment (vol.%)	<1	0.22	ASTM D 2709
Gross Heating Value (cal/g)	11411.4	9850.6	ASTM D 240

From Table 2.3, some significant differences were found between Reference (REF) and biodiesel fuel. These differences are within the daily differences typically found in samples taken from urban collectors, and, in any case, they did not lead to any significant difference in ultimate composition and to very small differences in the unsaturation level (iodine number). The reference fuel (REF) is a typical low sulphur diesel fuel similar to those available in Spanish petrol stations in winter. It was supplied by Repsol YPF, and fulfils the current European norm EN-590. (Magín Lapuerta, José M. Herreros, Lisbeth L. Lyons, Reyes García-Contreras and Yolanda Briceño, 2008)

Table 2.3: Specifications of biodiesel fuels

Properties	**REF**	**WCO**
Density at 15 °C (kg/m^3)	834	887
Kinematic viscosity at 40 °C (cSt)	2.72	5.16
Gross heating value (MJ/kg)	45.54	39.26
Lower heating value (MJ/kg)[a]	42.49	36.59
Acid number (mg KOH/g)	0.10	0.55
% C (wt.)	86.13	76.95[b]
% H (wt.)	13.87	12.14[b]
% O (wt.)	0	10.91[b]
Sulphur content (ppm wt.)	34	0[b]
Water content (ppm wt.)	57	466
IBP (°C)	172	320
T10 (°C)	211	325
T50 (°C)	270	333
T90 (°C)	340	356
Molecular weight	211.7[c]	293.2[b]
Stoichiometric fuel/air ratio	1/14.67	1/12.55
CFPP (°C)	−18	−6
Iodine number[b]	-	97.46
Renewable fraction	0	90.11[d]

[a] Calculated from composition and gross heating value.

[b] Calculated from speciation.

[c] Calculated by Aspen-Advisor software.

[d] Calculated from waste cooking oil composition.

From Table 2.4, it shows that biodiesel sample meet EN14214 standards for density, kinematic viscosity, copper corrosion, acid value, cetane number, free glycerol and total glycerol. There was slight difference in density and viscosity compared to diesel but completely acceptable. The higher flash-point of biodiesel sample is beneficial in safety aspect, and the low sulfur content is the reason for the extremely low SOx emission associated with its use as fuel. The cetane number is higher than diesel resulting in a smoother running of the engine with less noise. Biodiesel sample is an oxygenated fuel naturally with oxygen content about 10% which contributes to the favorable emission, but leads to a little bit low caloric value compared with petro-diesel. Biodiesel nearly meets all the properties of normal diesel fuel, according to diesel and EN14214 standards, which indicates that Biodiesel derived from WCO has adequate values compared to diesel fuel. (Xiangmei Meng, Guanyi Chen and Yonghong Wang, 2008)

Table 2.4: The properties of biodiesel sample compared to diesel fuel and EN14214 biodiesel standard

Parameter	Samples	Diesel fuel	EN14214
Density (15 °C, kg/m^3)	890	NA	860–900
Flash point (°C)	171	> 65	> 101
Kinematic viscosity (40 °C, mm^2/s)	4.23	3.0–8.0	3.5–5.0
Sulfur content (wt.%)	0.007	< 0.05	< 0.01
10% Conradson carbon residue	0.2	0.3	0.3

Copper strip corrosion (3 h, 50 °C)	1a	class1	class1
Water content (mg/Kg)	150	NA	< 500
Cold filter plugging point (°C)	1	≤ 4	NA
Free glycerol (%)	0.008	NA	0.02
Total glycerol (%)	0.21	NA	0.25
Acid value (mg KOH/g)	0.48	< 0.1	≤ 0.5
Cetane number	54.5	> 49	≥ 51
Caloric value (MJ/kg)	32.9	41.8	NA

2.1.3 Green House Gases and Global Warming Impacts and Benefits

Human-caused global warming is one of the greatest and most urgent challenges facing humanity and life on earth today. The main culprit is the enormous amount of the potent greenhouse gas carbon dioxide (CO_2) released into the atmosphere by the burning of fossil fuels (petroleum, coal, natural gas). Burning fossil fuels releases more than 6 billion tons of CO_2 per year, twice as much as the biosphere can absorb. The excess CO_2 is clogging the atmosphere, with the result that less solar heat is reflected away, more heat reaches the earth's surface, and global temperatures rise.

Using vegetable oils or animal fats as fuel for motor vehicles is in effect running them on solar energy. All biofuels depend on the conversion of sunlight to energy (carbohydrates) that takes place in the green leaves of plants. Plants use water and CO_2 from the atmosphere as the raw materials for making carbohydrates. Burning plant (or animal) products in an engine releases the CO_2 back into the atmosphere, to be taken up again by other plants. The CO_2 is recycled.

Natural mechanisms work to hold the amount of CO_2 in the atmosphere at a stable level, maintaining a balance between the CO_2 removed from the atmosphere to be "fixed" into growing organic matter and the CO_2 released back into the atmosphere when the organic matter burns or dies and decays. The net amount of CO_2 in the atmosphere stays the same. Activitities that don't disrupt this balance are described as carbon-neutral**.**

In fact, there's no actual reduction in the amount of CO_2 produced when biodiesel is burned instead of petrol-diesel. The same amount of CO_2 will come out of the exhaust pipe with either fuel. But the CO_2 released by burning biodiesel is part of the current natural cycle; it does not raise the level of CO_2 in the atmosphere and does not act as a greenhouse gas. Biodiesel is carbon-neutral and does not increase global warming.

Petrol-diesel is not carbon-neutral. Burning petrol-diesel unleashes CO_2 that has been trapped beneath the earth for millions of years, upsetting the natural balance and raising the level of CO_2 in the atmosphere, causing global temperatures to rise. Fossil-fuel CO_2 is an active greenhouse gas. In practice however, not all biodiesel is carbon-neutral. It depends how it's produced. "Life-cycle" studies of the whole production process from sowing the seed to filling the fuel tank can show a different picture.

Industrialised agricultural production of oil crops like soy or rapeseed depends heavily on fossil-fuel inputs which must be included in the equation, and biodiesel made from these crops is not carbon-neutral. But petrol-diesel is a lot worse. Organic farms don't use fossil-fuel-based chemical fertilizers and their fossil-fuel inputs are much lower, shrinking to zero when they produce their own fuel and energy on-farm, as a growing number of organic farmers are doing.

Biodiesel made from waste vegetable oil (WVO) should also qualify. Most WVO ends up in the sewers and landfills where it does no good and doesn't offset any fossil-fuel use. Converting it to biodiesel is a much better option, a social service. Reduce, reuse, and recycle. The US produces an estimated 4.5 billion gallons a year of used cooking oil, and most of it goes to waste. By comparison, US commercial production of biodiesel in 2006 was only 250 million gallons, most of it made from new soy oil, very little from used oil.

According to a model developed by the USA’s Argonne National Laboratory (ANL), neat (100%) biodiesel from soybeans can cut global warming pollution by more than half relative to conventional petroleum based diesel. The emissions benefits are higher for canola oil. In the future, non-conventional sources like algae may have the potential to provide dramatic (90%) reductions in global warming pollution. However, significant technological hurdles remain before algae and other advanced feedstocks can be processed into biodiesel for commercial purposes.

It is important to note that the ANL model of global warming impacts does not take into account changes in land use. When soybeans are used for fuel, they are taken out of the market for food. This increases prices and stimulates demand that farmers around the world respond to by bringing more land into cultivation. With soybean production increasing in the Amazon, it is possible that the lifecycle global warming pollution of soybean biodiesel is even higher than petroleum diesel, once indirect land use changes are considered.

When biodiesel is made from recycled food oil or other waste products these land use considerations do not apply. Also advanced technologies including biomass gasification may allow the use of other waste streams to be converted to synthetic diesel fuels, expanding the pool of potentially low carbon diesel. In addition to land use, there is also some controversy over the emissions impact of fertilizer use and other land use practices, such as tillage practices. As a result, the estimated emissions from biodiesel can be expected to change as our understanding of the lifecycle improves.

Large scale production of biodiesel would require more virgin plant oils or other waste stream sources to meet larger demands. However, such large-volume biodiesel use could raise concerns about genetically modified crops, pesticide use, and land-use impacts common to ethanol and all other plant-based fuels. Crops for biodiesel must be grown in a manner that supports wildlife habitat, minimizes soil erosion, avoids competition for food crops, and does not rely on the use of harsh chemicals and fertilizers.